Polymer Bulletin 40, 447–453 (1998)

Polymer Bulletin

Polymerization of cyclic monomers

6. Synthesis and radical polymerization of asymmetric disubstituted 2-vinylcyclopropmes

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Received: 14 November 1997/Accepted: 20 November 1997

Summary

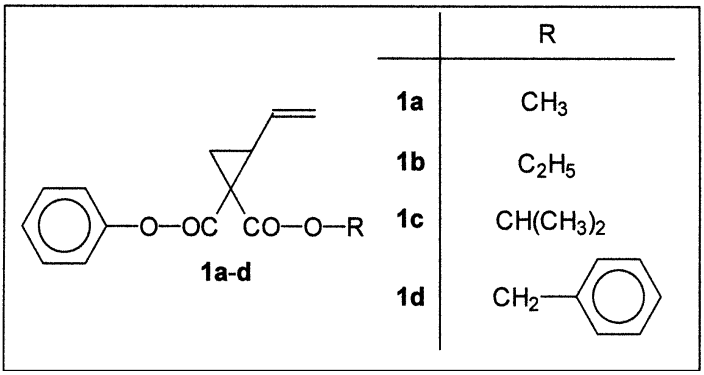
Asymmetric disubstituted 1-phenoxy-2-vinylcyclopropanes **1** were synthesized either by the esterification of the corresponding 1-alkoxycarbonyl-2-vinyicyclopropane-1-carboxylic acid with phenol or by the reaction of asymmetric malonates with trans-1,4-dibromo-2-butene. The structure of the new vinylcyclopropanes was confirmed by elemental analysis, IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The radical polymerization of the asymmetric substituted 2-vinylcyclopropanes in bulk with 2,2'-azoisobutyronitrile (AIBN) results in transparent polymers. The glass transition temperature of the formed polymers varries between 41 und 61 °C.

Introduction

2-Vinylcyclopropanes have been known as monomers which undergo radical ring-opening polymerization to result in polymers bearing mainly a 1,5-ring-opened unit1,2). The radical ring-opening polymerization of the crystalline 1,1-bis-(phenoxycarbonyl)-2-vinylcyclopropane shows an volume expansion of about 6 %3). A low polymerization shrinkage or even expansion in volume makes such monomers attractive as components for adhesives or composites. In this context, we reported about the synthesis and radical polymerization of monomers containing two or three polymerizable vinylcyclopropane moieties4). These cross-linking monomers generally show a higher polymerization rate and the corresponding polymers exhibit a better solvent resistance.

To further improve the mechanical properties of the polymers based on 1,1-disubstituted 2-vinylcyclopropanes, it is necessary to know more about the influence of the monomer structure on the glass transition temperature.

Previously, we reported about the synthesis and polymerization of 2-methylene-1,3-dioxepanes[5,6]. This paper describes the synthesis and radical polymerization of asymmetric substituted 1-phenoxy-2-vinylcydopropanes **1a-d**:



Experimental

Materials

Dimethyl and diethyl malonate, phenol, 1,4-trans-dibromo-2-butene (Aldrich), methylene chloride, methanol and tetrahydrofuran (THF) were dried over molecular sieves. 4-Dimethylaminopyridine (DMAP) and 1,3-dicyclohexylcarbo-diimide (DCC) were used without further purification. 2,2'-Azoisobutyronitrile (AIBN) was purified by recrystallization. All chemicals were purchased from Fluka. Isopropylphenyl and benzylphenyl malonate were prepared by esterification of the phenyl malonic acid with isopropanol and benzylalcohol, respectively, in the presence of DDC. 1-Methoxycarbonyl-2-vinylcydopropane-1-carboxylic acid was prepared according to procedure described eadier[4]. 1-Eth-oxycarbonyl-2-vinylcyclopropane-1-carboxylic acid was synthesized analogously.

Syntheses

Synthesis of 2-vinylcyclopropanes **(1a-b)** general procedure):

In a 100 mL three-necked flask with a magnetic stirrer, 9.4 (10.0 mmol) of the phenol 61 mg (0.5 mmol) of DMAP, and 11.0 mmol of 1-methoxy- (for **1a**), or 1-ethoxycarbonyl-2-vinylcydopropane-1-mrboxylic acid (for **1b**) were dissolved in 50 mL anhydrous methylene chloride. Then, 20.3 g (0.1 mol) of DCC was added to the stirred solution in portions, so that the temperature did not surpass 0-5 °C. After stirring for 6 h at room temperature, the formed precipitate was filtered off. The filtrate was washed with diluted HCI, aqueous $NaHCO_3$ solution, and brine, dried over anhydrous sodium sulfate and then evaporated. The crude product was purified by flash column chromatography (silica gel 60) with n-hexane/ethyl acetate (9:1) as the eluent. The evaporation of the filtrate in vacuo yielded the products as colourless oils:

1-Methoxycarbonyl-1-phenoxycarbonyl-2-vinylcyclopropane **(1a)**: Yield: 11.3 g (46%). $C_{14}H_{14}O4$ (246.26): Calc.: C 68.28, H 5.73; Found: C 67.50, H 5.58. IR (KBr, cm^{-1}): 2954 (w), 1738 (s), 1639 (w), 1594 (w), 1490 (m), 1438 (m), 1329

(m), 1264 (m), 1207 (s), 1119 (m), 799 (m) and 689 (m). ^{1}H NMR ($CDCl_3$, 90 MHz): δ = 1.55-1.95 (m;2H,$CH_{2,cyclopr.}$), 2.52-2.90 (m;1H,$CH_{cyclopr.}$), 3.73 (s;3H, CH_3-O), 5.06-5.85 (d;3H,-CH=CH_2), 7.03-7.70 (m;5H,CH_{phenyl}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.59 and 21.14 ($CH_{2,cyclopr.}$) 31.74 and 31.89 ($CH_{cyclopr.}$), 36.27 (>C<), 52.73 and 52.85 (CH_3-O), 119.11 and 119.22 (CH_2=), 120.95, 121.36, 126.05, 126.37,129.43 and 129.80 (CH_{phenyl}), 132.61 and 132.67 (=CH-), 150.63 150.76 (C_{phenyl}), 166.05, 167.50, 168.20 and 168.76 (C=O).

1-Ethoxycarbonyl-1-phenoxycarbonyl-2-vinylcyclopropane (**1b**): Yield: 15.1 g (57%), b.p.: 103-109 (mbar). $C_{15}H_{16}O_4$ (260.29): Calc.: C 69.22, H 6.20; Found: C 69.15, H 6,32. IR (KBr, cm $^{-1}$): 2983 (w), 1732 (s), 1639 (w), 1593 (w), 1493 (m), 1371 (m), 1318 (s, sh), 1263 (s), 1205 (s), 1162 (m), 1120 (s), 753 (m) and 688 (m). ^{1}H NMR ($CDCl_3$): δ = 1.29 (t;3H,-CH_3), 1.71-1.74 (m;1H,$CH_{2,cyclopr.}$), 1.85-1.88 (m;1H,$CH_{2,cyclopr.}$), 2.69-2.75 (m;1H,$CH_{cyclopr.}$), 4.21-4.29 (m;2H,-CH_2-CH_3) 5.18 and 5.35 (d;2x1H,=CH_2), 5.47-5.52 (m;1H, =CH-), 7.09-7.12 (m;2H, o-CH_{phenyl}), 7.21-7.25 (m;1H, p-CH_{phenyl}) and 7.35-7.39 (m;2H,m-CH_{phenyl}). ^{13}C NMR ($CDCl_3$): δ = 14.40 (CH_3), 21.36 ($CH_{2,cyclopr.}$), 31.65 ($CH_{cyclopr.}$), 36.27 (>C<), 61.72 (CH_2-O), 118.99 (CH_2=), 121.72, 126.02 and 129.15 (CH_{phenyl}), 132.96 (=CH-), 150.77 (C_{phenyl}), 166.96 and 168.34 (C=O).

Synthesis of 2-vinylcyclopropanes (**1c-d**) general procedure):

To a suspension of oil free sodium hydride 8.80 g (0.22 mol), 1,4-trans-dibromo-2-butene (11,76 g, 0,055 mol), and dry THF (150 mL, isopropylphenyl (for **1c**) or benzylphenyl malonate (for **1d**) (0.10 mol) in THF 150 mL was added drop-wise at ambient temperature under nitrogen atmosphere for 30 min. The mixture was heated at 65 °C for 4 h. Then, THF was removed under reduced pressure. The residue was dissolved in 200 mL diethyl ether, washed with aqueous sodium bicarbonate and then dried over anhydrous sodium sulphate. After the removal of diethyl ether in vacuo the crude product was either purified by fractionated distillation (**1c**) or by flash column chromatography (silica gel 60) with CH_2Cl_2 as the solvent (**1d**):

1-Isopropoxycarbonyl-1-phenoxycarbonyl-2-vinylcyclopropane (**1c**): Yield: 11.0 g (40%), b.p.: 109-117 °C (0.01 mbar). $C_{16}H_{18}O_4$ (274.32): Calc.: C 70.06, H 6.61; Found: C 67.56, H 6,60. IR (KBr, cm^{-1}): 2982 (m), 2122 (w,impurities), 1727 (s), 1639 (w), 1594 (w), 1492 (m), 1374 (m), 1359 (m), 1317 (s), 1272 s), 1202 (s), 1161 (m), 1125 (s), 1101 (s), 913 (m), 753 (m) and 688 (m). ^{1}H NMR ($CDCl_3$): δ = 1.22-1.32 (m;6H,-CH_3), 1.62-1.72 (m;1H,$CH_{2,cyclopr.}$), 1.77-1.82 (m;1H, $CH_{2,cyclopr.}$ 2.69-2.75 (m;1H,$CH_{cyclopr.}$), 4.21-4.29 (m;2H,-$C\underline{H}_2$-CH_3), 5.18 and 5.35 (d;2x1H,=CH_2), 5.10-5.58 (m;4H, CH_2=CH->CH-O-), 7.06-7.25 (m;5H,CH_{phenyl}), ^{13}C NMR ($CDCl_3$). δ = 20.34 and 20.86 (CH_3), 21.78 ($CH_{2cyclopr.}$), 31.24 and 31.50 ($CH_{cyclopr.}$), 36.10 (>C<), 69.34 and 69.62 (CH-O), 118.99 (CH_2=), 121.39, 126.00 and 129.46 (CH_{phenyl}), 132.75 (=CH-), 150.68 (C_{phenyl}), 166-50, 168.56 and 168.80 (C=O).

1-Benzyloxycarbonyl-1-phenoxycarbonyl-2-vinylcyclopropane (**1d**): Yield: 18.4 g (57%). $C_{20}H_{18}O_4$ (322.36): Calc.: C 74.52, H 5.63; Found: C 74.50, H 5.84. IR (KBr, cm^{-1}): 3094 (w), 1731 (s), 1638 (w), 1592 (m), 1493 (s), 1456 (m), 1380 (m), 1319 (s,sh), 1268 (s), 1199 (s,s), 1116 (s), 921 (m), 751 (m) and 697 (m). ^{1}H NMR ($CDCl_3$): δ = 1.68-1.76 (m;1H,$CH_{2,cyclopr.}$), 1.82-1.90 (m;1H,$CH_{2,cyclopr.}$), 2.73-2.78 (m;1H,$CH_{cyclopr.}$), 5.16-5.67 (m;5H,-OCH_2-/CH=CH_2) and 6.93-7.37 (m;10H, CH_{aryl}). ^{13} C NMR ($CDCl^3$): δ = 20.70 and 21.13 ($CH_{2,cyclopr.}$), 31.61 and 31.96 ($CH_{cyclopr.}$), 35.89 (>C<), 67.48 (CH_2-O), 118.76, 121.30, 125.95, 127.90, 128.30,

129.34, 132.79 and 135.41 (C_{benzyl}/CH_{phenyl}/CH_2=CH), 150.49 (C_{phenyl}), 166.01, 166.86, 168.13 and 179.07 (C=O).

Polymerization

Radical bulk polymerization was carried out in sealed glass tubes as previously described[7]. The obtained bulk polymerizates were diluted with $CHCl_3$. Then, the polymer solutions were precipitated in cold methanol or in a mixture of methanol with water (vol. ratio 9:1). The polymer was filtered off and then dried to constant weight in vacuum.

Poly(**1a**): IR (KBr, cm^{-1}): 3044 (w), 2954 (m), 1769 (sh,s), 1740 (s), 1592 (m), 1492 (m), 1194 (s), 1163 (s), 742 (m) and 687 m. ^{1}H NMR ($CDCl_3$): δ = 1.89-2.78 (br,m;4.6H,-CH_2-/$H_{Cyclobut.}$), 3.73 (s;3H,-OCH_3), 5.39-5.54 (m;1.4H,-CH=) and 7.01-7.35 (m;5H,CH_{Phenyl}). ^{13}C NMR ($CDCl_3$): δ = 35.85 (CH_2 53.05 (OCH_3), 58.22 ($C_{aliph.}$), 121.73, 126.48, 129.11 and 129.89 (CH_{Phenyl}/-CH=), 150.89 (C_{phenyl}), 169.64 and 171.10 (C=O).

Poly(**1b**): IR (KBr, cm^{-1}): 2983 (m), 2932 (m), 1737 (s), 1594 (m), 1490 (m), 1194 (s), 1164 (s), 745 (m) and 687 (m). ^{1}H NMR ($CDCl_3$): δ = 0.88-1.25 (m,3H,-CH_3) 1.85-2.77 (br,m;4.9H,-CH_2-/$H_{Cyclobut.}$), 4.11-4.23 (m;2H,-OCH_2), 5.44-5.54 (m;1.1H,-CH=) and 7.02-7.34 (m;5H,CH_{phenyl}). ^{13}C NMR ($CDCl_3$): δ = 14.21 (CH_3), 35.91 (CH_2), 57.53 ($C_{aliph.}$), 61.60 (OCH_2), 121.31, 126.00, 128.69 and 129.47 (CH_{phenyl}/-CH=), 150.57 (C_{Phenyl}), 168.33 and 170.13 (C=O).

Poly(**1c**): IR (KBr, cm^{-1}): 3042 (w), 2983 (m), 2937 (m), 1765 (sh,s), 1734 (s), 1594 (m), 1492 (m), 1190 (s), 1164 (s), 744 (m) and 688 m. ^{1}H NMR ($CDCl_3$): δ = 1.16-1.22 (m,6H,-CH_3), 1.1.77-2.88 (br,m;4.9H,-CH_2-/$H_{Cyclobut.}$), 5.06-5.08 (m; 1H,-OCH<), 5.40-5.55 (m;1.1H,-CH=) and 7.00-7.38 (m;5H,CH_{Phenyl}). ^{13}C NMR ($CDCl_3$): δ = 22.13 (CH_3), 36.35 (CH_2), 57.98 ($C_{aliph.}$), 69.58 (OCH<), 121.67, 126.34, 129.00 and 129.86 (CH_{Phenyl}/-CH=), 150.96 (C_{Phenyl}), 169.75 and 169,93 (C=O).

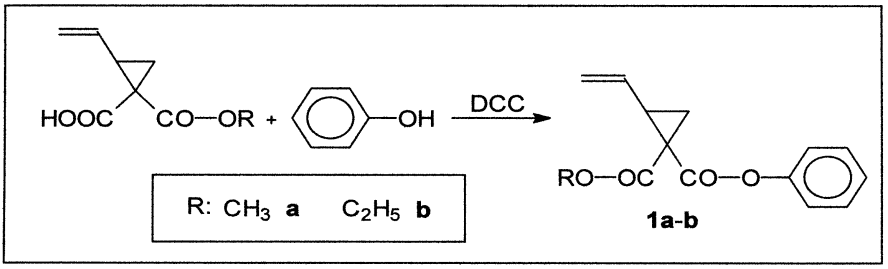
Poly(**1d**): IR (KBr, cm^{-1}): 3035 (w), 2955 (m), 1766 (sh,s), 1736 (s), 1592 (m), 1492 (m), 1194 (s), 1160 (s), 740 (m) and 690 m. ^{1}H NMR ($CDCl_3$): δ = 1.91-2.79 (br,m;4.8H,-CH_2-/$H_{cyclobut.}$), 5.16 (s;2H,-OCH_2-), 5.31-5.51 (m;1.2H,-CH=) and 6.92-7.37 (m;10H,CH_{aryl}). ^{13}C NMR ($CDCl_3$): δ = 36.06 (CH_2), 58.18 ($C_{aliph.}$), 67.64 ($CH_{2,benzyl}$), 121.74, 125.92, 129.00 and 129.78 (CH_{aryl}/-CH=), 135,36 (C_{benzyl}), 150.89 (C_{Phenyl}), 169.53 and 170.33 (C=O).

Measurements

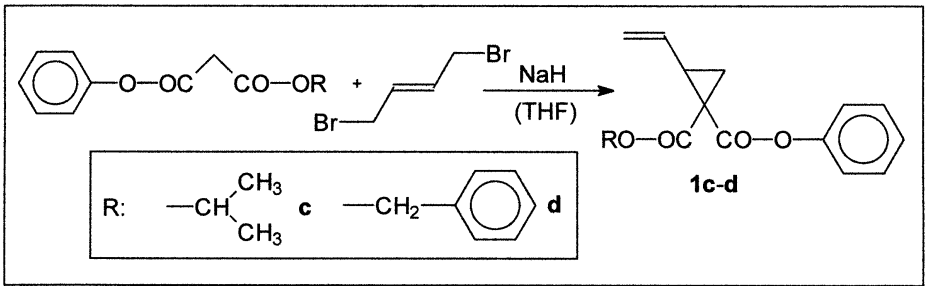
NMR measurements were recorded on an EM 390 (Perkin-Elmer, 90 MHz) or a DPX-400 spectrometer (Bruker, 400 MHz) using tetramethylsilane (JMS) as the standard and $CDCl_3$ as a solvent. A FT-IR spectrometer 1600 (Perkin-Elmer) was used to record IR spectra. The number-average molecular weights of the polymers was determined by gel permeation chromatography (GPC) using THF as the eluent, a UV-detector Spectra 100 and columns calibrated with poly(styrene) standards. Differential scanning calorimetry (DSC) measurements were performed by using a Perkin-Elmer DSC-7 thermal analyzer. A scanning rate of 10 °C/min was used. The elemental analyses were performed with an elemental analyzer EA 1108 (Fisons Instr.).

Results and discussion

The monomers **1a** and **1b** were synthesized by esterification of 1-methoxycarbonyl- and 1-ethoxycarbonyl-2-vinylcyclopropane-1-carboxylic acid with phenol in the presence of DCC:



The monomers **1c** and **1d** were prepared by the reaction of the corresponding asymmetric malonates with trans- 1,4-dibromo-2-butene in the presence of sodium hydride:



The monomers **1a-d** are viscous liquids. The characterization of the new vinylcyclopropanes was carried out by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis. The spectroscopic data are in agreement with the expected structure. For example, the formation of the 2-vinylcyclopropane unit is supported by the presence of a multiplett assignable to >CH- of the cyclopropane ring δ = 2.69-2.75 ppm, two dupletts assignable to CH_2= of the vinyl group at δ = 5.18 and 5.35 ppm in the ^{1}H NMR spectrum of **1b**. Furthermore, the ^{13}C NMR spectra of the obtained monomers show that they are probably mixtures of *EIZ*-isomers.

The bulk polymerization of the monomers **1a-d** was carried out in the presence of AIBN at 65 °C. The radical vinyl polymerization of 2-vinylcyclopropanes **1a-d** resulted in highly viscous transparent polymerizates. (Tab. 1). The polymer yield varied between 70.0% (**1b**) and 82.7% (**1d**), whereas the number-average molecular weight of the formed polymers was between 19000 and 47000 g/mol.

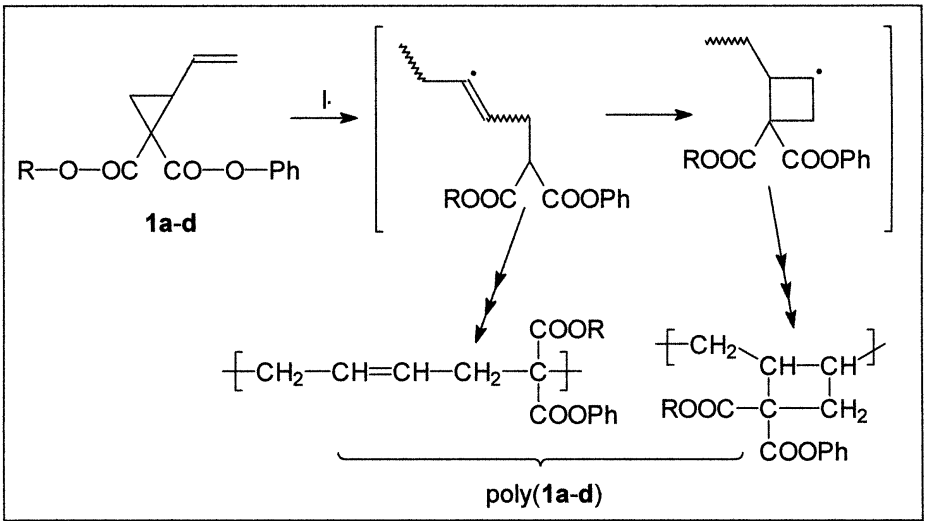
Furthermore, the results show that the monomer structure influences the glass transition temperature (T_G) of the formed polymer. The T_G decrease in the following order: poly(**1a**) > poly(**1c**) > poly(**1b**) > poly(**1d**). It is surprising that the lowest T_g was found for poly(**1d**). Poly(1,1-bis(phenoxycarbonyl)-2-vinylcylopropane), obtained in the presence of AIBN, shows a T_G of 77 °C[3]). That means

Table 1: Bulk polymerization of 2-vinylcyclopropanes **1a-d** in the presence of AIBN (2.5 mol-%) at 65 °C

Monomer	Polymer yield (%)	$M_n \times 10^{-3}$ (g/mol)	T_G (°C)
1a	79.1	19.0	61
1b	70.0	21.0	54
1c	74.3	47.0	57
1d	82.7	33.0	41

that the introduction of a methylene group between only one ester and phenyl group significantly disturbs the aromatic-aromatic interaction and results in a T_G-decrease of 26 °C.

In principle, 2-vinylcyclopropanes undergo radical polymerization to result in a polymer consisting of a 1,5-ring-opened unit and a cyclobutane unit. The ^{1}H NMR spectra of polymers obtained in the presence of AIBN clearly indicate the formation of the 1,5-adduct unit. Typical signals of the polymers assignable to the ring-opened structure, for example in case of poly(**1d**), are broad peaks at 1.89-2.78 (-CH_2-) and the peak at 5.39-5.54 ppm (-CH=) in the ^{1}H NMR spectrum. Based on the ratio of the intensity of the (-CH=-peak to the (CH_{aryl})-peak the calculated content of the 1,5-adduct units varies between about 55 and 70 mol %.



In contrast to this, it is very difficult to assign the signals of the cyclobutane ring in the ^{1}H NMR or ^{13}C NMR spectra because they are too broad to distingish. This was also reported previoulsy by Sugiyama[3] or Sanda[8] in case of other poly(2-vinylcyclopropane)s.

In the next paper, we will report about the synthesis and radical polymerization of difunctional 1-alkoxycarbonyl-2-vinylcyclopropanes with an arylene spacer between the two polymerizable 2-vinylcyclopropane groups.

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